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6 April 1992

Dr. George Wright
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Office of the Chief of Naval Research
800 North Quincy Street
Arlington VA 22217-5000

Dear Dr. Wright,

Enclosed is my Final Technical Report for the Contract N00014-91-J-1265, covering the funding period 1/1/91 to 1/1/92. Although the original Contract was for "First-Principles Computational Studies of Si/Noble-Metal Interfaces", I have previously notified you, in a letter dated 16 September 1991, of a change in focus to study the electronic structure of the new class of high-temperature superconductors, the alkali-doped C_{60} fullerides. The computational methods used were identical to those described in the original Contract. The enclosed Report only discusses research I have done on the fulleride materials.

Finally, I wish to thank you for your time and support of this research. I hope to be working with you again in the future.

Sincerely,

Steven C. Erwin

cc:
Administrative Grants Officer, ONR
Director, Naval Research Laboratory
Defense Technical Information Center

Final Technical Report
for
Contract No. N00014-91-J-1265

First-principles computational studies of alkali-doped C_{60} fullerides

PROGRAM: Post-tenure research by NRC-NRL research associates (cf. ONCR INSTRUCTION 3912.1)

INSTITUTION: Department of Physics
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FUNDING PERIOD: 1 Jan 1991 - 1 Jan 1992

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   a. Fullerenes and alkali-doped fullerides

   b. Diamond interfaces and surfaces

1. Summary of fullerene research during the funding period

In the spring of 1991, researchers at AT&T Bell Laboratories reported the discovery of superconductivity at 18 K in a potassium-doped fullerene solid, K_xC_{60}.[1] This marked a major turning point in the young history of the C60 molecule "buckminsterfullerene": from a hypothetical molecule[2] (1985), to small-scale (mg) production of crystalline powders[3] (1988), to large-scale synthesis[4] (1990), to a material with the highest transition temperature of any molecular superconductor.

Of course, this history represents only one of many research lines. Concurrently with the work at AT&T on partial doping, researchers at the Laboratory for Research on the Structure of Matter at the University of Pennsylvania were doping solid C_{60} to saturation with potassium. The resulting pure phase, K_6C_{60}, was characterized by x-ray diffraction in April 1991: the lattice was body-centered cubic, with the C_{60} molecules essentially undistorted, orientationally ordered, and each surrounded by a cage of 24 K atoms.[5] Nothing was known about the electronic structure at this early stage.

To address this issue I immediately began, in collaboration with researchers at the Naval Research Laboratory, first-principles electronic-structure calculations for K_6C_{60}, using our gaussian-orbital LDA method.[6] Within two weeks, the answer was in hand:[7] the ground state of K_6C_{60} is insulating, with an indirect gap of 0.48 eV. The band structure is quite similar to that of undoped solid C_{60}, with the fully ionized K 4s electrons donated into the 3-fold degenerate C π-electron band. The implication of this finding is that, in contrast to the weak van der Waals forces that are responsible for cohesion in pure C_{60}, bonding in K_6C_{60} is almost entirely ionic. Furthermore, it is apparent that each C_{60}

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[1] A.F. Hebard *et al.*, Nature **350**, 600 (1991).
[2] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature **318**, 162 (1985).
[3] R.M. Fleming et al., in *Materials Research Society Symposium Proceedings*, Vol. 206, p. 691. (Materials Research Soc., Pittsburgh, 1991).
[4] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, Nature **347**, 354 (1990).
[5] O. Zhou *et al.*, Nature **351**, 462 (1991).
[6] S.C. Erwin, M.R. Pederson, and W.E. Pickett, Phys. Rev. B **41**, 10437 (1990).
[7] S.C. Erwin and M.R. Pederson, Phys. Rev. Lett. **67**, 1610 (1991).

binds 6 extra electrons; this unusually high charge state is stabilized by the surrounding electrostatic cage of 24 K^+ ions. These theoretical predictions were subsequently confirmed by photoemission[8] and optical absorption.[9]

By early summer, x-ray diffraction experiments for the superconducting phase—by then known to be K3C60—revealed a face-centered cubic lattice with K atoms filling all the available tetrahedral and octahedral interstitial sites.[10] With this structural information, we performed the first *ab initio* band-structure calculations for K_3C_{60}.[11] Again, the bands were found to be quite similar to those of the undoped phase, with the C-derived conduction band half-filled by 3 excess electrons from the K^+ ions. Assuming the fullerene molecules to be orientationally ordered leads to a complicated multi-sheeted Fermi surface (experiment suggests that two possible orientations, rotated by 90° with respect to each other, are populated randomly in 1:1 proportion). The first is free-electron-like, and the second (which holds the superconducting carriers) is multiply connected, forming two distinct symmetry-equivalent surfaces. The calculated clean-limit London penetration depth of 1600 Å corresponds to a dirty-limit value in the range 3000-3500 Å; this is in reasonable agreement with experiment, falling midway between the reported values of 1600 Å (lower critical-field measurements[12]) and 4800 Å (muon-spin relaxation[13]). Our calculation also provided the first theoretical predictions for the Fermi-level density-of-states, $N(E_F)=13.2$ states/eV and the Fermi velocity, $v_F=1.8\times10^7$ cm/s. Experimental determinations of $N(E_F)$ do not yet agree among themselves, ranging from 3.8 states/eV (photoemission[14]) to 34 states/eV (NMR[15]). No direct experimental tests of the Fermi-velocity prediction have yet been reported.

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[8]G.K. Wertheim *et al.*, Science **252**, 1419 (1991).
[9]T. Pichler, M. Matus, J. Kürti, and H. Kuzmany, Solid State Commun. **81**, 859 (1992).
[10]P.W. Stephens *et al.*, Nature **351**, 632 (1991).
[11]S.C. Erwin and W.E. Pickett, Science **254**, 842 (1991).
[12]K. Holczer *et al.*, Phys. Rev. Lett. **67**, 271 (1991).
[13]Y.J. Uemura *et al.*, Nature **352**, 605 (1991).
[14]C.T. Chen *et al.*, Nature **352**, 603 (1991).
[15]R. Tycko *et al.*, Phys. Rev. Lett. **68**, 1912 (1992).

Most recently, we have turned our attention to normal-state transport properties of K_3C_{60}.[16] Using the lowest-order variational solution to the Bloch-Boltzmann scattering equation, valid in the limit of purely electron-phonon scattering, Allen *et al.*[17] have derived explicit formulae for the resistivity, Hall coefficient, and thermopower. These quantities involve various integrals over the Fermi surface, for which we have used our electronic-structure results of Ref. 11. By using the measured intensity from inelastic neutron scattering to calculate the electron-phonon scattering rate, we find that the temperature dependence of the resistivity is essentially linear down to 50 K, with a slight supralinear behavior from 50-500 K; this is in qualitative agreement with preliminary measurements on single crystal samples.[18] The room temperature resistivity is predicted to be roughly 1 mΩ-cm.

The Hall coefficient, R^H, is traditionally interpreted as giving the number and sign of the charge carriers. In the Bloch-Boltzmann variational solution, R^H is a complicated measure of the average curvature of the Fermi surface; this quantity reduces to 1/n (n=carrier density) in the free-electron case. In the isotropic scattering-time approximation, the temperature dependence of the Hall coefficient drops out; we have calculated a value $R^H=0.70 \times 10^{-8}$ m^3/C (in a free-electron model, this corresponds to 0.65 hole carriers per formula unit). Single-crystal measurements of R^H have not yet been done; film measurements give a strongly temperature dependent R^H with a room-temperature value roughly 1/5 of ours.[19]

[16] S.C. Erwin and W.E. Pickett, Phys. Rev. Lett. (submitted).
[17] P.B. Allen, Phys. Rev. B **17**, 3725 (1978); B. Chakraborty, W.E. Pickett, and P.B. Allen, Phys. Rev. B **14**, 3227 (1976); P.B. Allen, W.E. Pickett, and H. Krakauer, Phys. Rev. B **47**, 7482 (1988).
[18] X.D. Xiang (private communication).
[19] T.T.M. Palstra, R.C. Haddon, A.F. Hebard, and J. Zaanen, Phys. Rev. Lett. **68**, 1054 (1992).

2. Summary of current fullerene research

I am currently following several different lines of fullerene work. An on-going collaboration with experimentalists and theorists at the University of Pennsylvania examines adsorption of C_{60} molecules on metal surfaces. The relevant questions include: What are the possible stable charge states of the fullerene molecule? How does the relative stability of these states depend on the metal work function? How are the electronic and vibrational levels perturbed by the metal surface? Preliminary theoretical work indicates that C_{60}^{+2} is the highest stable charge state possible for any of the common alkali metals, regardless of the work function. An account of our work to date is in press.[20]

A second line of work concerns K_4C_{60}.[21] This material, which may be the only line phase compound other than K_3C_{60} that is not a band insulator, is somewhat problematic. Although band theory results for C_{60}, K_3C_{60}, and K_6C_{60} are all in good agreement with various experimental probes, K_4C_{60} represents a total failure. First-principles LDA band structure results predicts that K_4C_{60} should be metallic, with a Fermi-level DOS higher than that of K_3C_{60}.[21] NMR experiments show unambiguously that K_4C_{60} is an insulator.[22] The reason for this discrepancy is unclear: speculations include the possibility of a Mott-Hubbard metal-insulator transition or a charge-density-wave (CDW) ground state. I favor the latter explanation. The structure of K_4C_{60} is body-centered tetragonal, with c/a=0.90; hence there is somewhat greater coupling between molecules along the c-axis, relative to the coupling in the ab-plane. This is reminiscent of a 1-dimensional metal, which is generally subject to a Peierls distortion along the chain. Moreover, my calculation of the Fermi surface of K_4C_{60} finds 3 sheets; two are closed

[20] E. Burstein, S.C. Erwin, M.Y. Jiang, and R.P. Messmer, Physica Scripta (to appear).
[21] A preliminary account of this work will appear in S.C. Erwin, in *Buckminsterfullerenes*, edited by W.E. Billups and M.A. Ciufolini (VCH Publishers, 1992) (to appear).
[22] D.W. Murphy, M.J. Rosseinsky, R.M. Fleming, R. Tycko, A.P. Ramirez, R.C. Haddon, T. Siegrist, G. Dabbagh, J.C. Tully and R.E. Walstedt, preprint.

spheres, and the 3rd consists of essentially flat sheets in the ab-plane. Calculation of the charge susceptibility reveals a moderately strong nesting vector $Q=\pi/a(0,0,1)$, precisely what is needed for a Fermi-surface-driven instability leading to CDW formation. This would lead to a doubling of the unit cell and open up the possibility of a metal-insulator transition. Unfortunately, the energetics of CDW formation are extremely subtle, arising primarily from electron-electron correlation effects that are inadequately described by LDA.[23] Nevertheless, one can investigate the effect that various cell doublings would have on the band structure (which should be well-described by LDA), in effect searching for a structure with an insulating ground state. This requires accurate first-principles calculations of unit cells containing 128 atoms (2×60 C atoms and 2×4 K atoms). These calculations are beyond the current capabilities of plane-wave and augmented-plane-wave methods; with the Gaussian-orbital method, however, they are quite manageable, and represent an ideal proving ground for what I believe will be the next generation of electronic-structure methods.

[23] A.W. Overhauser, in *Electron Correlations in Solids, Molecules, and Atoms*, edited by J.T. Devreese and F. Brosens (Plenum, 1983), p. 41.

3. Papers published during the funding period

Fullerenes and alkali-doped fullerides

Erwin, S.C. and Pederson, M.R. Electronic Structure of Crystalline K_6C_{60}. Phys. Rev. Lett. **67**, 1610 (1991).

Erwin, S.C. and Pickett, W.E. Theoretical Fermi-Surface Properties and Superconducting Parameters for K_3C_{60}. Science **254**, 842 (1991).

Pederson, M.R., Erwin, S.C., Pickett, W.E., Jackson, K.A., and Boyer, L.L. Electronic structure of fullerenes: isolated molecules and metal-doped crystals. Proc. International Symp. on the Physics and Chemistry of Finite Systems (Richmond, VA, 1991).

Burstein, E., Erwin, S.C., Jiang, M.Y., and Messmer, R.P. The charge state and electronic structure of C_{60} (Buckminsterfullerene) molecules adsorbed on a metal surface: Theoretical considerations. Physica Scripta (to appear).

Erwin, S.C. Electronic structure of the alkali-doped fullerides. In *Buckminsterfullerenes*, edited by W.E. Billups and M.A. Ciufolini (VCH Publishers, 1992) (to appear).

Erwin, S.C. and Pickett, W.E. Theoretical normal-state transport properties of K_3C_{60}. Phys. Rev. Lett. (submitted).

Diamond interfaces and surfaces

Pickett, W.E., Pederson, M.R., Jackson, K.A., and Erwin, S.C. Theoretical studies of diamond surface chemistry and diamond-metal interfaces. In *Wide Bandgap Semiconductors*, edited by T.D. Moustakas, J.I. Pankove, and Y. Hamakawa (Mat. Res. Soc., 1991).

Erwin, S.C. and Pickett, W.E. Vanishing Schottky barriers in diamond/metal interfaces. Solid State Communications **81**, 891 (1992).

4. Presentations

Fullerenes and alkali-doped fullerides

Fermi surface of superconducting K_3C_{60}: First-principles calculations, S.C. Erwin, Workshop on Fullerites and Solid-State Derivatives, University of Pennsylvania, 2-3 August 1991.

Theoretical electronic structure of alkali-doped fullerenes, S.C. Erwin and M.R. Pederson, International Symposium on the Physics and Chemistry of Finite Systems: From Clusters to Crystals, Richmond VA, 8-12 October 1991.

Fermi surface of K_3C_{60}: electronic properties of the normal and superconducting states, S.C. Erwin, University of Pennsylvania, 20 November 1991.

Fermi surface of K_3C_{60}: electronic structure and superconductivity, S.C. Erwin, W.E. Pickett, and M.R. Pederson, Materials Research Society 1991 Fall Meeting, Boston, 1-6 December 1991.

Theoretical normal-state transport properties of K_3C_{60}, S.C. Erwin and W.E. Pickett, APS General Meeting, Indianapolis, 16-20 March 1992.

Studies of electron-lattice coupling in fullerides using an accurate tight-binding method, D.A. Papaconstantopoulos, W.E. Pickett, M.R. Pederson, and S.C. Erwin, APS General Meeting, Indianapolis, 16-20 March 1992.

Diamond interfaces and surfaces

Schottky-barrier suppression in diamond/metal interfaces, S.C. Erwin and W.E. Pickett, APS General Meeting, Cincinatti, 17-21 March 1991.

Schottky-barrier suppression in diamond/metal interfaces, S.C. Erwin and W.E. Pickett, 179th Meeting of the Electrochemical Society, Washington DC, 5-10 May 1991.

Schottky barriers at diamond/nickel interfaces, S.C. Erwin and W.E. Pickett, Diamond Conference 1991, Oxford, UK, 7-10 July 1991.

Theory of Schottky barriers in diamond/metal interfaces, S.C. Erwin, American Chemical Society National Meeting, New York, 25-30 August 1991.

Theoretical studies of the role of interface orientation in diamond/metal Schottky barriers, S.C. Erwin, 12th European Conference on Surface Science, Stockholm, Sweden, 9-12 September 1991.

Theory of interfaces involving diamond and cubic boron nitride, W.E. Pickett, M.R. Pederson, K.A. Jackson, and S.C. Erwin, Materials Research Society 1991 Fall Meeting, Boston, 1-6 December 1991.